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RELATIVE BAND OSCILLATOR STRENGTHS FOR CARBON MONOXIDE: A ${}^1\Pi-X\,{}^1\Sigma^+$ TRANSITIONS

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ABSTRACT

Band oscillator strengths for CO transitions between the electronic states A ${}^1\Pi$ and X ${}^1\Sigma^+$ were measured via absorption with a synchrotron radiation source. When referenced to the well-characterized (5, 0) band oscillator strength, our relative values for the (7, 0) to (11, 0) bands are most consistent with the recent experiments of Chan et al. and the theoretical predictions of Kirby & Cooper. Since the results from various laboratory techniques and theory now agree, analyses of interstellar CO based on absorption from A–X bands are no longer hindered by uncertainties in oscillator strength.

Subject headings: ISM: molecules — molecular data — ultraviolet: ISM

1. INTRODUCTION

Carbon monoxide is the second most abundant molecule in interstellar space. Its ubiquitous radio emission delineates the location of molecular clouds. In cloud envelopes, the abundance of CO is determined primarily from measurements at ultraviolet wavelengths. A particularly useful set of transitions for such studies includes the system of bands involving the A ${}^1\Pi$ electronic state and the $v = 0$ level in the ground state X ${}^1\Sigma^+$. For instance, A–X transitions seen in the spectrum of ζ Ophiuchi (Sheffer et al. 1992; Lyu, Smith, & Bruhweiler 1994; Lambert et al. 1994) were used to probe the physical conditions of the gas. In order to extract reliable information on physical conditions, however, well-characterized band oscillator strengths are needed to convert the amount of absorption into column densities (see Lambert et al. 1994). The available data on oscillator strengths for especially useful, relatively weak bands show a dispersion of some 30%, which is larger than the quoted uncertainties and which is too large for the quality of data being acquired with the *Hubble Space Telescope*. In this paper, we present new results on relative band oscillator strengths that help to clarify the situation.

The available theoretical and experimental results reveal discordant oscillator strengths for A–X ($v', 0$) transitions with $v' \geq 7$. The results of Eidelsberg et al. (1992), which are based on an absorption experiment of modest spectral resolution with a synchrotron source, are 20%–30% larger than other determinations. These include measurements involving electron impact excitation (Lassettre & Skerbele 1971; Chan, Cooper, & Brion 1993) and a more recent set of absorption measurements (Smith et al. 1994), as well as the theoretical determination of Kirby & Cooper (1989). We performed an experiment in many ways similar to the one of Eidelsberg et al. (1992) in order to ascertain whether the systematic differences were the result of the technique. This has consequences beyond the study of interstellar CO because a large body of work on photoabsorption is based on moderate resolution data. We obtained relative band oscillator strengths, which are especially important for studies on the abundances of ${}^{12}\text{CO}$ and ${}^{13}\text{CO}$, that are consistent with all but those of Eidelsberg et al. (1992).

2. EXPERIMENTAL DETAILS

The absorption experiment in the vacuum ultraviolet was conducted at the Synchrotron Radiation Center of the University of Wisconsin—Madison, where the 1 m Aluminum Seya-Namioka (Al-Seya) beamline was used. The Al-Seya was interfaced with a 486 IBM PC for scanning and data collection. The spectral resolution (FWHM) with 25 μm slits was ≈ 0.30 Å; this value depends weakly on the beam current. Carbon monoxide gas (spectroscopic grade, Spectra Gases, Inc.) was introduced to a gas cell with LiF windows sealed by O-rings. The separation of the two windows, which determines the length of the absorption cell, was set by an accurately machined stainless steel spacer of 2.63 ± 0.01 mm. The cell and gas lines were evacuated, outgassed, and backfilled with CO at room temperature prior to each measurement. The desired pressures ranging from 30 mtorr to 1000 mtorr were measured with a calibrated capacitive manometer (Baratron 127A, MKS Inc.) to ± 1 mtorr while monitoring the cell temperature to ± 0.5 K with a thermocouple gauge. Owing to the mechanical pump used in our experiment, the base pressure was ~ 2.5 mtorr. The flux of synchrotron radiation through the gas cell was measured by a Hamamatsu R1220 photomultiplier with a CsTe cathode and a MgF_2 window. The anode current of the photomultiplier tube (PMT) was converted to a voltage and digitized by a computer data acquisition card. At a PMT voltage of 1000 V, this detection system was linear over the range of signal levels measured in our experiment. Before taking a CO absorption spectrum, the background spectrum due to the dark current was determined and later removed from the sample spectrum.

A typical experiment covered the wavelength range between 1175 and 1435 Å in intervals of 75 Å. Each interval contained at least one A–X band in common with adjacent intervals, thereby providing a check on stability on timescales of minutes. In our measurements, the step size between points was 0.05 Å and the time period to collect each point was set at 0.04 s. Each point included an integration of 400 samples for a readout. At least four spectra were recorded for each set of experimental conditions and for each wavelength interval. In all, some 500 spectra were acquired.

3. ANALYSIS AND RESULTS

The transmittance spectra for each band head, corrected for dark current, were summed numerically with appropriate

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TABLE 1
THE MEASUREMENTS

Pressure (mtorr)	W_λ (5, 0) (mÅ)	W_λ (7, 0) (mÅ)	W_λ (8, 0) (mÅ)	W_λ (9, 0) (mÅ)	W_λ (10, 0) (mÅ)	W_λ (11, 0) (mÅ)
30	39.68 ± 1.47	9.21 ± 1.45	6.63 ± 1.63
50	66.66 ± 1.99	16.63 ± 1.11	8.82 ± 0.92	3.28 ± 1.05
100	116.1 ± 2.0	34.83 ± 1.52	18.61 ± 0.82	7.98 ± 1.37	5.08 ± 0.87	...
200	175.0 ± 2.2	72.05 ± 2.46	39.19 ± 1.22	17.03 ± 1.86	7.07 ± 0.70	2.72 ± 0.84
300	215.5 ± 2.6	97.54 ± 2.87	53.13 ± 1.48	24.63 ± 2.00	8.34 ± 1.01	2.76 ± 1.03
400	251.0 ± 2.4	118.1 ± 2.6	69.61 ± 1.54	35.20 ± 2.06	17.50 ± 1.42	6.21 ± 1.99
500	260.4 ± 3.9	131.8 ± 3.5	77.37 ± 2.45	38.47 ± 2.86	16.56 ± 2.06	6.07 ± 1.77
600	290.0 ± 2.6	153.5 ± 2.0	93.87 ± 1.73	49.95 ± 2.37	23.46 ± 1.29	11.68 ± 2.05
700	301.1 ± 3.0	163.3 ± 2.5	104.2 ± 2.0	55.31 ± 2.38	26.41 ± 1.85	10.06 ± 1.70
800	175.5 ± 2.5	117.6 ± 2.0	61.00 ± 2.82	30.79 ± 1.82	10.80 ± 1.86
1000	200.7 ± 3.3	133.0 ± 2.3	76.23 ± 3.40	38.85 ± 2.34	17.71 ± 2.45

wavelength corrections, if necessary, to account for slight shifts of the grating calibration between spectra. The equivalent width W_λ for each band was extracted from the spectra with NOAO's IRAF package. The results for each band and pressure are displayed in Table 1. [Severe blending with triplet-singlet transitions prevented us from analyzing the (4, 0) and (6, 0) bands.] The oscillator strength for each vibrational band at each pressure studied was derived from these measurements of W_λ through comparison with synthetic profiles (see Lambert et al. 1994).

The synthetic spectra were based on spectroscopic data for each vibrational band of the $A-X$ electronic transition of CO (Tilford & Simmons 1972). The synthetic spectra were convolved with a Gaussian instrumental bandpass of 0.30 Å in order to match the experimental spectrum. Each synthetic spectrum then was adjusted to match the experimental spectrum in a nonlinear least-squares fitting procedure with the band oscillator strength, the rotational excitation temperature T_{ex} for the $v = 0$ level of the ground state, and the wavelength offset as free parameters.

In order to perform the synthesis, the CO column density was required. The column density at pressures from 30 mtorr to 700 mtorr were obtained from a fit to the (5, 0) band with the oscillator strength of Chan et al. (1993). (All previous determinations of band oscillator strength for $v' = 0-6$ agree with each other at the 5%–10% level.) As a check, we also calculated the column density from the measured CO pressure, the temperature, and the absorption path length. The pressure and temperature of the absorption cell were used to determine the CO number density n in units of molecules cm^{-3} under the reasonable assumption that CO was acting as an ideal gas. (For our pressure range, the results are essentially identical to those derived using the van der Waals equation of state.) This number density was multiplied by the absorption path length to arrive at a column density. The two determinations for pressures between 400 and 700 mtorr agreed with each other at the 5% level, consistent with the uncertainties in the oscillator strength of Chan et al. (1993). For lower pressures, the two determinations differed by up to 30%, with the fitted value being smaller. We attribute the cause of the difference to an impurity gas, probably water. We estimate an approximate contribution of 10 mtorr from the impurity gas at all pressures because the differences decrease with increasing pressure and become negligible at 400 mtorr. The final synthetic spectrum was plotted together with the experimental spectrum for visual confirmation of the fit; examples are illustrated in Figure 1. The oscillator strengths (f -values)

derived from this procedure (with the fitted column densities) are listed in Table 2. Of particular importance for interstellar studies is knowledge of the relative band oscillator strengths, as discussed by Lambert et al. (1994). In Table 3, we show the

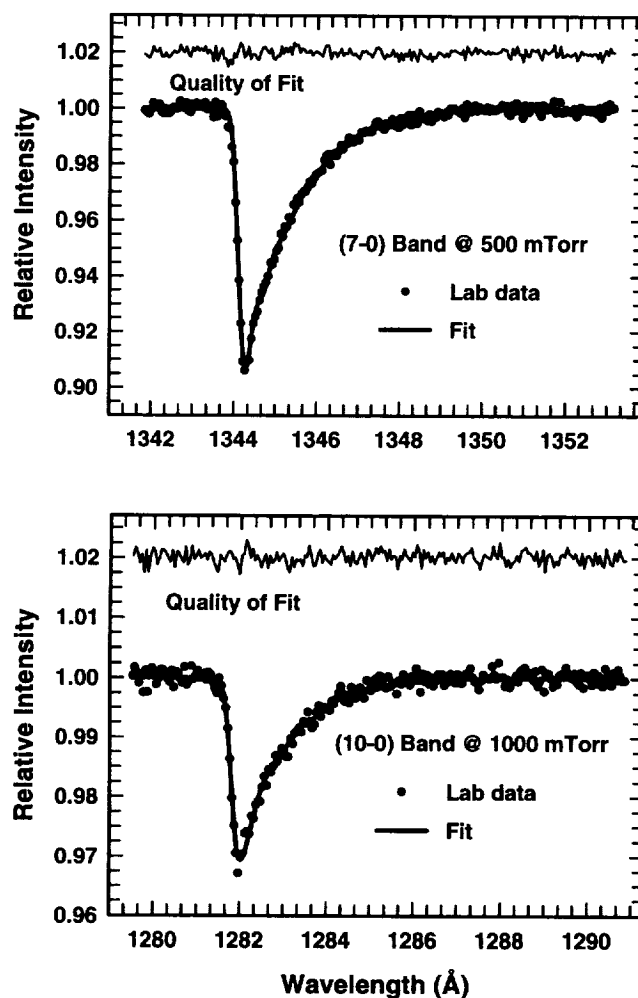


FIG. 1.—Synthetic profiles of CO bands. The measurements are represented by filled circles, the fitted spectrum by the thick solid line, and the root mean square differences between the measurements and the fit by a thin solid line, where no difference occurs at 1.02 on the relative intensity scale. Spectra of the strong (7, 0) band taken at 500 mtorr and of the weak (10, 0) band at 1000 mtorr are shown.

TABLE 2
OSCILLATOR STRENGTHS

Pressure (mtorr)	$f(7, 0)$ (10^{-3})	$f(8, 0)$ (10^{-3})	$f(9, 0)$ (10^{-3})	$f(10, 0)$ (10^{-3})	$f(11, 0)$ (10^{-3})
30.....	3.47 ± 0.94	2.37 ± 0.90
50.....	3.39 ± 0.45	1.79 ± 0.31	0.60 ± 0.27
100.....	3.51 ± 0.31	1.84 ± 0.16	0.77 ± 0.19	0.49 ± 0.12	...
200.....	3.90 ± 0.28	1.93 ± 0.13	0.81 ± 0.13	0.35 ± 0.05	0.14 ± 0.06
300.....	3.60 ± 0.24	1.74 ± 0.11	0.79 ± 0.10	0.27 ± 0.05	0.07 ± 0.04
400.....	3.51 ± 0.21	1.70 ± 0.10	0.81 ± 0.08	0.39 ± 0.05	0.13 ± 0.06
500.....	3.56 ± 0.22	1.68 ± 0.11	0.78 ± 0.09	0.32 ± 0.06	0.11 ± 0.05
600.....	3.41 ± 0.18	1.59 ± 0.09	0.78 ± 0.06	0.35 ± 0.03	0.16 ± 0.04
700.....	3.33 ± 0.18	1.61 ± 0.09	0.76 ± 0.06	0.34 ± 0.04	0.13 ± 0.03
800.....	3.47 ± 0.19	1.68 ± 0.09	0.76 ± 0.06	0.35 ± 0.03	0.12 ± 0.03
1000.....	3.62 ± 0.20	1.65 ± 0.09	0.79 ± 0.06	0.37 ± 0.04	0.16 ± 0.03
f_w^a	3.51 ± 0.19	1.69 ± 0.09	0.78 ± 0.05	0.35 ± 0.02	0.13 ± 0.02

^a The f -value based on a weighted average for each pressure determination. The error includes systematic effects at the 5% level (see text).

band f -values relative to that of the (5, 0) band, which we find to be $(14.5 \pm 0.8) \times 10^{-3}$; other determinations are included for comparison.

4. DISCUSSION

In light of the differences in the oscillator strengths for the $A-X(v', 0)$ bands with $v' \geq 7$ among the available determinations, we designed our experiment so that optically thick lines from unresolved rotational structure were not encountered. A key ingredient in our experiment was the use of a short absorption path length and relatively low CO pressures. This combination allowed us to measure CO column densities comparable to those seen in interstellar cloud envelopes—i.e., $\sim 10^{15} \text{ cm}^{-2}$. Since the measurements occurred at $\approx 298 \text{ K}$, the absorption involved many rotational levels ($j = 0-20$), which helped to minimize the optical depth for a specific rotational transition.

We also examined a number of potential problems associated with our analysis. Two of the authors (S. R. F. and J. B. S.) measured the W_λ for each band via independent methods and codes. S. R. F. aligned and summed the experimental profiles for a band acquired at a specific pressure, and he fit the continuum to a low-order spline. J. B. S. measured each W_λ with a linear fit to the continuum, and the final W_λ for a band at a given pressure was a weighted average of the individual W_λ . The results for W_λ agreed to within their mutual errors. The data in Table 1, used in the rest of the analysis, are

based on the values of S. R. F. because this method allowed us to detect weaker absorption. Second, we verified that our spectral resolution was 0.30 \AA by synthesizing spectra with proposed instrumental widths ranging from 0.25 to 0.40 \AA and then comparing the various fits. As noted above, we examined the appropriateness of the column density used in the synthesis. Finally, we did not assume a Boltzmann distribution for the ground-state rotational levels. In all cases, we found T_{ex} was less than 298 K , with values ranging from $237 \pm 22 \text{ K}$ at 30 mtorr to $277 \pm 3 \text{ K}$ at 1000 mtorr . In essence, at the low pressures used in our measurements, radiative decay of high-lying rotational levels was quicker than collisional deexcitation. The fact that the band oscillator strengths are tightly constrained regardless of pressure (see Table 2) gives us confidence in our methodology.

The last row in Table 2 shows the band oscillator strength as a weighted average of the individual results for pressure. In doing these averages, a 5% error due to systematic effects was added to the errors in W_λ , pressure, and column density. The main reason for inclusion of systematic effects is that although our f -values are consistent with other recent results (e.g., Chan et al. 1993; Smith et al. 1994) at the $2-3 \sigma$ level, they are typically 15% lower than the other experimental determinations. The theoretical results of Kirby & Cooper (1989) lie between our f -values and those of Chan et al.

As noted by Lambert et al. (1994), a useful way of checking the consistency of the interstellar results for ^{12}CO and ^{13}CO

TABLE 3
RELATIVE OSCILLATOR STRENGTHS WITH RESPECT TO THE (5, 0) BAND

BAND	R					
	(FML) ^a	(LS) ^b	(ERBT) ^c	(CCB) ^d	(DM) ^e	(KC) ^f
7, 0.....	0.242 ± 0.019	0.28 ± 0.02	0.36 ± 0.06	0.29 ± 0.02	0.29 ± 0.08	0.29
8, 0.....	0.117 ± 0.009	0.14 ± 0.01	0.18 ± 0.03	0.14 ± 0.01	0.15 ± 0.04	0.14
9, 0.....	0.054 ± 0.005	0.070 ± 0.005	0.086 ± 0.017	0.066 ± 0.007	0.065 ± 0.016	0.067
10, 0.....	0.024 ± 0.002	0.032 ± 0.002	0.040 ± 0.007	0.028 ± 0.003	0.029 ± 0.008	0.030
11, 0.....	0.009 ± 0.002	0.016 ± 0.001	0.017 ± 0.003	0.012 ± 0.002

^a The present paper.

^b Lassetre & Skerbele 1971.

^c Eidelsberg et al. 1992.

^d Chan et al. 1993.

^e Davies & Mason 1995.

^f Kirby & Cooper 1989.

relies on relative band f -values. They note that their astronomical data provide consistent results when the laboratory determinations of Lassettre & Skerbele (1971) or Chan et al. (1993) are incorporated into the analysis. (The same applies if the theoretical results of Kirby & Cooper [1989] are considered.) Such was not the case when the f -values of Eidelsberg et al. (1992) are used. As shown in Table 3, our relative f -values are in excellent agreement with those of Chan et al. (1993), whose f -values yielded the best curves of growth for the astronomical data (Lambert et al. 1994). The agreement between our results and the relative f -values of Lassettre & Skerbele (1971); Kirby & Cooper (1989), and Davies & Mason (1995) is also good. The relative band oscillator strengths of Eidelsberg et al. (1992) differ appreciably from ours and the others. Since we also acquired moderate-resolution absorption data, the cause for the difference cannot lie in the technique but lies elsewhere in the analysis such as in their extrapolation to zero pressure.

5. CONCLUSION

We have performed an absorption experiment to extract precise relative oscillator strengths for $A-X$ bands in CO. Our results agree with earlier experimental results based on electron impact excitation (Chan et al. 1993), with astronomical

results (Lambert et al. 1994), and with the theoretical work of Kirby & Cooper (1989). Although the experiment of Eidelsberg et al. (1992) is the most similar to ours, their reported f -values do not lead to similar relative band oscillator strengths. The fact that our results are consistent with the other measures indicates that the discrepancy does not lie with the technique. The most important conclusion of our study is that the recently determined f -values of Chan et al. (1993) (and their relative strengths) should be used for other interstellar studies, as suggested by Lambert et al. (1994). Since the compilation by Morton & Noreau (1994) of line f -values for $A-X$ transitions is based on the work of Chan et al., this source includes the most appropriate data for analyses of CO absorption above 1200 Å.

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